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Corrosion of electrodeposited zinc-manganese alloys

M Selvam and S Guruviah

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

Zinc-manganese alloys of different compositions, (2-55% manganese, rest zinc) deposited from a sulfate/citrate bath, were used to study their corrosion in 3% sodium chloride solution of three different pHs (pH 5.0, 7.0 and 9.0) and in 1 mol. sodium hydroxide solution. Mainly electrochemical methods were used to study their corrosion and the results obtained are discussed. Deposits containing 2-25% manganese show very low corrosion rate in 3% sodium chloride solution and those with 25% Mn show very low corrosion rate in alkaline solution.

Key words: Alloy plating, sulfate/citrate bath, Zn-Mn alloys

INTRODUCTION

Steel plated with zinc and its alloys provide good corrosion resistance [1–5]. Among the various zinc based alloys, alloy with manganese produced from sulfate/citrate bath also affords excellent corrosion protection and other properties [1–5]. The reported corrosion studies show that log of time for appearance of rust is related linearly to manganese content of the coating upto 60%, beyond which it increases insignificantly [5]. A detailed study has been made and reported by the present authors on zinc-manganese alloy deposition [6]. The present work deals with corrosion studies of zinc-manganese (2-55%) alloy, deposited from the developed bath, in 3% sodium chloride solutions of three different pHs (pH 5.0, 7.0 and 9.0) and in 1 mol. sodium hydroxide solution.

EXPERIMENTAL

A sulfate/citrate bath [6] was used to deposit zinc-manganese alloys of different compositions (2-55% manganese). Usual pretreatment procedure was used for mild steel to coat this alloy. Coated samples of thicknesses varying from 20 to 30 μm were suitably masked to get known area and subjected to corrosion studies. Corrosion data such as i_{corr}, E_{corr}, R_p and corrosion rate were obtained from the corrosion tests which include Tafel extrapolation, small amplitude cyclic voltammetry (SACV), linear polarisation, weight loss, potential-time and current-time measurements. The details of the experimental techniques are discussed elsewhere [7]. Tafel extrapolation was used as the basis for corrosion rate calculation.

RESULTS AND DISCUSSION

The corrosion rate of the alloy containing 2.4% manganese is more or less the same as zinc. When the manganese content is above 15%, the corrosion rate is reduced in chloride medium at all pH values investigated, whereas the corrosion rate of manganese in chloride medium at acidic or neutral pH values is high. This may probably be due to unfavourable structure and composition of the corrosion products of manganese in presence of chloride ions. However, when a mixture of oxides/chlorides of zinc and manganese are formed, the alloy corrodes sacrificially and the effect of chloride ion on the nature of corrosion product is not so much. The corrosion products may be rich in zinc oxide with a higher volume.

In chloride medium, at pH 9.0, the corrosion rate of manganese is less than that of zinc, whereas the zinc-manganese alloys have corrosion rate equal to or better than manganese. Quite possibly the corrosion products of manganese and zinc-manganese alloys may contain oxides and hydroxides of manganese which are stabilised in this pH domain. The colour of corrosion product is brownish black, indicating the presence of Mn_3O_4, and Mn_2O_3, which may form a film unattacked by alkali and thereby enhancing the resistance to corrosion. However the E_{corr} values for zinc, zinc-manganese alloys and manganese in chloride corrosive media lie in the range of -1.03V to -1.267V (vs SCE), i.e. they lie in the more negative region. (Table I).

When one looks at the E_{corr} values of zinc and zinc-manganese (2.4%) alloy in 1 mol. sodium hydroxide, they are close to -1.4V (vs SCE) and therefore should behave similarly. But the E_{corr} values of zinc- manganese (14.3%) and that of manganese in 1 mol. sodium hydroxide are in the range of -0.036 to -0.545V (SCE) which are closer to E_{corr} of iron (-0.375V vs SCE) in this medium. This may be due to the nature of the oxide film formed on the surface by the corrosion products of manganese. Probably in alkaline medium, the potential quickly drifts towards less negative values from an initially high negative value as the corrosion products of manganese oxides grow on the

TABLE–I: Corrosion data for zinc-manganese alloy in 3% neutral sodium chloride solution

Coating	Tafel extrapolation				SACV	
	E_{corr} (V)	I_{corr} (μA)	Corr. rate (mpy)	Linear polarisation $1/R_p \times 10^{-3}$ ohm^{-1}	$(1/R_p \times 10^{-3}$ ohm$^{-1})$	Cdl
Manganese	−1.267	175.0	86.78	150.0	94.0	5690
Zinc	−1.035	80.0	47.88	40.0	45.0	2300
Mild steel	−0.618	27.3	12.5	3.8	5.3	7230
Zinc-manganese (2.4% Mn)	−1.037	35.0	20.85	27.4	28.0	18750
Zinc-manganese (14.3% Mn)	−1.043	26.0	15.11	23.8	26.0	15630
Zinc-manganese (24.8% Mn)	−1.046	27.0	15.34	12.5	24.5	17500
Zinc-manganese (37.5% Mn)	−1.048	33.0	18.33	21.0	23.0	15000
Zinc-manganese (54.1% Mn)	−1.058	41.0	22.07	11.0	20.0	13700

surface to produce a tenacious stable film in presence of OH^- ions.

CONCLUSION

Presence of manganese in the alloy coatings shifts the potentials of the parent metal towards more negative values. When manganese content is below 15% in zinc-manganese alloys, these alloys behave like zinc in offering cathodic protection to steel by sacrificially corroding in chloride medium. The nature and structure of the corrosion product of zinc is modified by oxides of manganese so that the zinc-manganese coatings offer better protection to steel than that of zinc in pure alkaline solutions. The protective properties of films formed by corrosion products are determined not only by their composition but also by their volume and tenacity.

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